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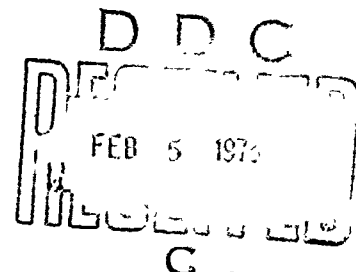# INVESTIGATION OF THERMOCHEMICAL EFFECTS ON BLOWOFF OF REENTRY VEHICLE HEATSHIELD RESINS

Larry D. Nichols

Moleculon Research Corporation

TECHNICAL REPORT NO. AFWL-TR-72-199

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## AIR FORCE WEAPONS LABORATORY

Air Force Systems Command

Kirtland Air Force Base

New Mexico

AFWL-TR-72-199

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
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INVESTIGATION OF THERMOCHEMICAL EFFECTS
ON BLOWOFF OF REENTRY VEHICLE HEATSHIELD RESINS

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FOREWORD

This report was prepared by the Moleculon Research Corporation, Cambridge, Massachusetts, under Contract F29601-72-C-0015. The research was performed under Program Element 61102H, Project 5710, Subtask AA105, and was funded by the Defense Nuclear Agency (DNA).

Inclusive dates of research were October 1971 through May 1972. The report was submitted 13 October 1972 by the Air Force Weapons Laboratory Project Officer, Mr. C. David Newlander (DYV).

This technical report has been reviewed and is approved.


C. DAVID NEWLANDER
Project Officer


CHARLES S. LEE
Major, USAF
Chief, Radiation Response Branch

JOHN K. LEROHL
Colonel, USAF
Chief, Technology Division

ABSTRACT

(Distribution Limitation Statement B)

Demonstration of a clear correlation between measureable thermodynamic properties and the impulsive momentum developed during blowoff would place predictive techniques on a more secure foundation and might make possible the formulation of resins with thermochemical properties specifically chosen for minimum blowoff damage. To find such a correlation, a set of modified phenolic resins was prepared which had similar elemental compositions and physical properties, but which differed strongly in their thermochemical parameters. Exposure of these samples on the Ion Physics Corporation Neptune B electron facility, with measurement of impulse by ballistic pendulum, yielded data which displayed a linear correlation between heats of decomposition and an additive term in the $E_n$ functic derived from measured impulses through simple BBAY theory. Evidence was also found for a broadening of the electron deposition profile at early times. The techniques developed here are applicable to a larger set of sample materials, and particularly to resins of more practical interest.

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# SECTION I

## INTRODUCTION

There is continuing debate over the direct influence of chemical factors on impulsive front surface vaporization, or blowoff. While it is accepted that single and mixed phase equations of state, by definition, govern the coupling between the deposited energy and the induced momentum and pressure, the chemistry implicit in these equations is generally subordinated to physical and hydrodynamic considerations. Approximation of chemical effects by a few empirical parameters still leads to a situation which taxes predictive techniques.

Chemical approximations first took the form of a constant sublimation energy, $E_s$, which represented the energy per unit mass required, for whatever reasons, to convert the solid to a vapor, and which could be subtracted from the local deposited energy to find the residue available for adiabatic work. This approach eventually proved inadequate and was replaced by a function, $E_n(E)$, which accounts for the energy not available for blowoff and is assumed to depend only on the deposited energy density $E$. Reasonable $E_n$ functions were usually able to reconcile theory with experiment, and this approach has been incorporated into many present blowoff impulse codes.

Although designed to take chemical factors into account, $E_n$ has never been clearly correlated with sample chemistry. This correlation should be demonstrable, and in fact it should be possible to derive $E_n$ directly from measurable chemical and thermochemical properties. This would strengthen the foundation of the whole predictive program, explain many discrepancies, and allow selection of better materials with optimized chemical properties.

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This program was undertaken to investigate the correlation between $E_n$ and sample thermochemistry, without attempting the much more difficult task of deriving $E_n$ directly from chemical principles. In most past studies, the role of chemistry has been obscured by large variations in nonchemical properties, but it is entirely feasible to prepare resins which differ significantly only in their detailed chemical structure. Even with elemental composition and density held virtually constant, differences of hundreds of calories per gram can be achieved in fundamental thermochemical parameters. Such a set of modified phenolic resins has now been prepared and subjected to momentum measurements under impulsive electron deposition. Subsequent modified BBAY calculations reveal that a strong relationship exists between thermochemistry and $E_n$.

The positive results obtained strongly point to the application of this technique to a larger number and variety of materials, together with a detailed thermodynamic analysis to extract all possible information on the processes and species which dominate the vaporization process.

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# SECTION II

## SAMPLE RESINS

Phenolic resins are formed by dehydrative condensation of a phenol
with an aldehyde, and their chemistry is described fully in the literature.
They lent themselves to this study because many compounds other than phenols
can participate in the condensation process, yielding modified resins in which
the modifiers are an integral part of the resin structure and should participate
homogeneously in vaporization. The resin system chosen was phenol/formaldehyde,
and the modifiers were methyl carbamate, $C_2H_5NO_2$, a stabile resin component,
and nitroethane, also $C_2H_5NO_2$, a much less stable, more energy rich resin
component. Monsanto SC-1008 was carried through as a comparison and control.

Estimated heats of formation indicated that resins prepared from 39
parts of phenol, 26 parts of modifier and 53 parts of formaldehyde, with
elimination of about 20 parts of water, would span a range of about 400
calories per gram in chemical heat content, depending on the modifier, while
retaining adequate physical properties. This was confirmed in practice,
though the final resins were somewhat hard and brittle. The identical
elemental composition and similar reactivity of the two modifiers allowed
the use of either alone, or any blend, with little effect on final com-
position or density.

At least three modified resins were needed to allow interpretation
of the test data, and these were chosen to span a large range of thermo-
chemical properties. Type A contained only methyl carbamate as modifying,
type B contained equal parts of methyl carbamate and nitroethane, and

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type C only nitroethane. Liquid pre-resins were prepared, and cured in small cups at moderate temperatures over a period of several weeks, with final curing in a vacuum oven. Evolved water must be allowed to diffuse out during cure or excessive internal pressures are generated. Samples cured in a week or less invariably cracked or developed bubbles.

The SC-1008 was fully cured until no further weight loss occurred, while the modified resins were cured to about 19 percent weight loss based on the liquid pre-resin. So long as the pre-resins were carefully prepared, total weight loss had been found to be a good criterion of final composition, and the good analytical results confirm this. The final composition of SC-1008 was found to depend on the precise curing procedure; rapidly cured SC-1008 probably contains evolved but unescaped water. The SC-1008 samples used here were cut from a single slab of slowly cured resin, and should be compared only with other samples of similar analysis. The resins were left unfilled, in order to emphasize any thermochemical differences.

The cured resins were machined into disks about 0.1" thick and 1.0" in diameter. Machining was done on a carefully cleaned, oil-free lathe, and the turnings were used to obtain elemental and thermal analyses on material from the actual test specimens. Specimens were measured and weighed to determine their densities, and individually epoxied into lucite holders 2" in diameter and 0.5" thick. Each holder was made with a well conforming to the dimensions of its intended sample. The cured and mounted samples were weighed to 0.01 milligram, and the front surface of the holder and specimen was mapped to 0.1 mil with a precision depth gage. Figures 1 through 3 show mounted samples. Densities, compositions and heats of

FIGURE 1. Photograph Showing Sample (Resin Type A) Epoxied into Lucite
Holder

FIGURE 1. Photograph Showing Sample (Resin Type A) Epoxied into Lucite Holder

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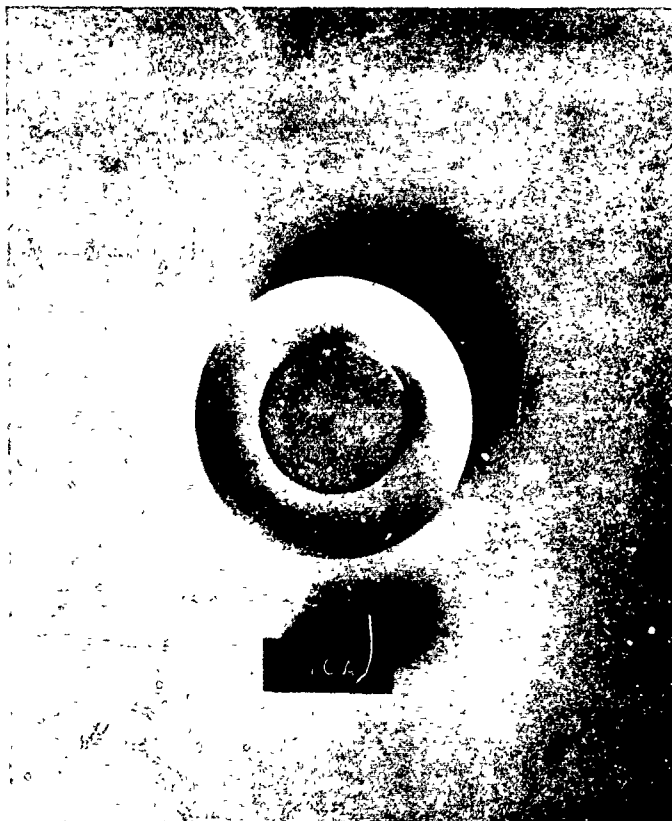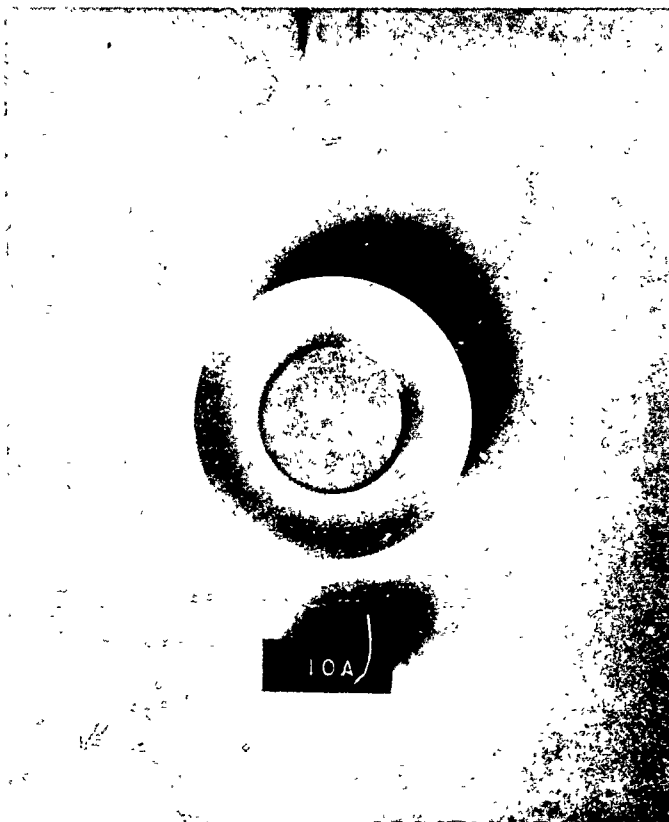FIGURE 2. Photograph Showing Sample (Resin Type B) Epoxied into Lucite
Holder

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FIGURE 3. Photograph Showing Sample (Resin Type C) Epoxied into Lucite
Holder

combustion are presented in Table I. Most but not all of the actual test
samples were analyzed, and some data are included in Table I for a few
samples not included in the final test set. These data are still of value
in establishing average values for these highly similar materials. The
oxygen analyses given in Table I are obtained by difference, as the analyses
were performed for carbon, hydrogen and nitrogen only.

The variations in chemical and thermodynamic properties among the samples
of the same resin could not be determined within the scope of the program.
The scatter in the impulse results may have arisen from such differences.
Each type of resin was therefore treated as having a single average com-
position and heat of combustion, and the analytic data were used to determine
the best averages.

Since analyses are prone to cluster about true values, within the
precision of the analytic techniques, or else show substantial error due to
some flaw such as incomplete combustion, the data were averaged by discarding
the extremes and averaging the remainder. For set B, with eight data points,
the two highest and the two lowest were discarded; for sets A and C, with
seven data points each, the single highest and lowest were discarded along
with the remaining most discrepant value; and for SC-1008, with four data
points, only the single most discrepant was rejected. These methods were
found to suppress all highly questionable individual values, such as the
heat of combustion of sample 31. Final average analyses are given in
Table II.

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## TABLE I

### Sample Properties

| Sample Number | Type | Elemental Analysis | | | | Density gm/cm$^3$ | $H_c$ cal/gm |
|---|---|---|---|---|---|---|---|
| | | %C | %H | %N | %O | | |
| 9 | A | 59.01 | 5.98 | 4.88 | 30.13 | 1.299 | 5772 |
| 10 | A | 57.81 | 6.31 | 4.86 | 31.02 | 1.308 | 5677 |
| 11 | A | 57.79 | 6.30 | 4.79 | 31.12 | 1.289 | 5667 |
| 12 | A | 57.73 | 6.20 | 4.75 | 31.32 | 1.283 | 5661 |
| 13 | A | 57.54 | 6.31 | 4.72 | 31.43 | 1.303 | 5689 |
| 14 | A | 58.40 | 6.10 | 4.82 | 30.68 | 1.322 | 5758 |
| 15 | A | 58.68 | 6.15 | 4.74 | 30.43 | 1.311 | 5748 |
| 42 | B | 58.77 | 5.87 | 4.25 | 31.11 | 1.292 | 5847 |
| 43 | B | 57.84 | 6.17 | 4.38 | 31.61 | 1.301 | 5854 |
| 50 | B | 57.41 | 6.27 | 4.11 | 32.21 | 1.318 | 5816 |
| 54 | B | 57.69 | 6.09 | 4.14 | 32.08 | 1.312 | 5773 |
| 55 | B | 58.06 | 6.42 | 4.10 | 31.42 | 1.311 | 5784 |
| 57 | B | 58.42 | 6.13 | 4.30 | 31.15 | 1.316 | 5836 |
| 59 | B | 58.51 | 6.23 | 4.15 | 31.11 | 1.316 | 5823 |
| 60 | B | 58.18 | 6.21 | 4.22 | 31.39 | 1.319 | 5836 |
| 31 | C | 60.11 | 6.01 | 4.19 | 29.69 | 1.320 | 6402 |
| 32 | C | 60.38 | 5.86 | 4.36 | 29.40 | 1.314 | 6239 |
| 34 | C | 60.34 | 6.13 | 4.12 | 29.41 | 1.316 | 6224 |
| 35 | C | 60.26 | 6.13 | 4.17 | 29.44 | 1.325 | 6118 |
| 36 | C | 59.72 | 5.97 | 3.88 | 30.43 | 1.315 | 6053 |
| 37 | C | 59.73 | 5.90 | 3.92 | 30.45 | 1.307 | 6093 |
| 40 | C | 59.88 | 5.90 | 3.88 | 30.34 | 1.319 | 6144 |
| 100 | SC-1008 | 77.44 | 5.97 | 0.39 | 16.20 | 1.231 | 7757 |
| 101 | SC-1008 | 77.03 | 6.13 | 0.30 | 16.54 | 1.227 | 7744 |
| 102 | SC-1008 | 77.34 | 6.58 | 0.17 | 15.91 | 1.228 | 7779 |
| 106 | SC-1008 | 75.84 | 5.98 | 0.14 | 18.04 | 1.231 | 7766 |

## TABLE II

## Average Resin Properties

| Resin Type | Elemental Analysis | | | | Density $gm/cm^3$ | $H_c$ cal/gm | $E_{H_2O}$ cal/gm | $E_{CO}$ cal/gm |
|---|---|---|---|---|---|---|---|---|
| | %C | %H | %N | %O | | | | |
| A | 57.93 | 6.24 | 4.78 | 31.05 | 1.305 | 5695 | −311 | +299 |
| B | 58.12 | 6.18 | 4.19 | 31.51 | 1.314 | 5828 | −464 | +154 |
| C | 60.15 | 5.95 | 4.10 | 29.80 | 1.316 | 6145 | −632 | − 47 |
| SC-1008 | 77.27 | 6.03 | 0.20 | 16.50 | 1.228 | 7761 | −397 | − 74 |

It made little numerical difference whether the derived thermochemical quantities were calculated for the individual samples and then averaged, or calculated directly from the average values. The latter simpler technique was employed. Two such derived quantities, $E_{H_2O}$ and $E_{CO}$, are included in Table II and require some explanation. To find a correlation between impulse and thermochemistry it is necessary to use thermochemical parameters which might be expected to show such a correlation. Within BBAY theory, the effect must enter through the absorption or release of chemical energy during dissociation and recombination. Since the modified resins have similar elemental compositions, prolonged high temperatures should convert them into the same final products. This may or may not occur at the modest energies and times typical of blowoff. If conversion to similar end products occurs, the energies absorbed or released by the different resins will differ by amounts which are independent of the specific products produced.

Thus one can begin the search for a correlation between thermochemistry ar $E_n$ by using the energy required to convert each resin into any specified set of products. It is reasonable to use a set of products which approximates what one would expect to find in a real blowoff vapor. From resins containing only carbon, hydrogen, nitrogen and oxygen one would expect only traces of surviving hydrocarbons and small amounts of carbon dioxide and oxides of nitrogen. The dominant species should be elemental carbon, hydrogen and nitrogen, along with water and/or carbon monoxide. There is enough carbon and hydrogen present for the oxygen to occur entirely as water, or entirely as carbon monoxide, or as any mixture. In the presence of hot excess carbon, carbon monoxide should be preferred, but phenolic resins are more likely to decompose initially into water than into carbon monoxide,

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and the system may not stay hot enough, long enough, for this water to react with the excess particulate carbon.

The simplest resolution of this uncertainty was to derive two thermochemical parameters for each resin: $E_{H_2O}$, the energy required to convert the resin into its elements plus water, and $E_{CO}$, the energy required to convert it into its elements plus carbon monoxide. These are also presented in Table II. There are many slightly different sources for the thermodynamic quantities used in calculating such heats of conversion. Those used here come from Air Force TO 11A-1-34, and include a correction for the heats of combustion from constant volume to constant pressure.

## SECTION III

## TESTING

The test plan was based on the use of the Ion Physics Corporation Neptune B facility operating near 200 keV, with momentum measurement by a ballistic pendulum. Two dose levels were desirable, the lower at about twice the minimum adequate to cause blowoff, and the higher as high as possible consistent with survival of the samples and measurement of momentum. Preliminary tests showed that a maximum dose of about 1000 cal/gm with a 0.5" diameter spot size, obtained by taping a carbon mask with a .5" diameter hole in it directly onto the sample, gave incipient rear-surface spall from the holder and extensive delamination of the adhesive bond, but produced specimens which could still be accurately measured post-test. This dose, corresponding to a fluence of about 45 $cal/cm^2$, was adopted as the higher value. The anticipated energy densities for incipient blowoff were in the range from 200 to 300 cal/gm, so a maximum dose of about 500 cal/gm was chosen for the lower value. This corresponded to a fluence of about 25 $cal/cm^2$. The actual electron beam spectrum used is shown in Figure 4.

Tests were performed on three consecutive days, and twenty-eight samples were irradiated. The first shattered itself and the carbon mask used to define the beam. This problem did not recur after replacement by a thicker mask, but four other samples failed to yield useful data due to various instrumental malfunctions, and one was tested under modified conditions.
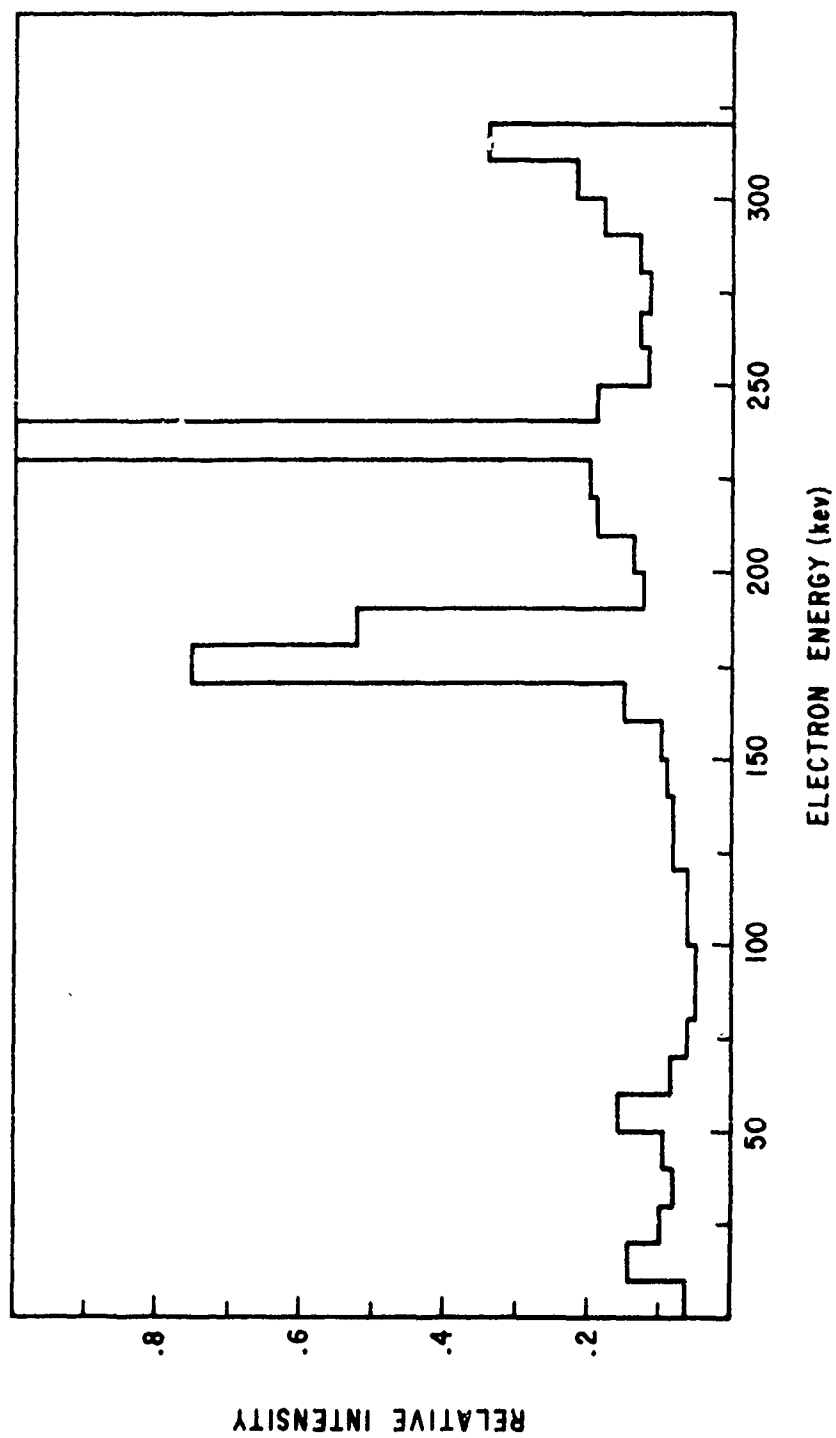
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Figure 4. Actual Electron Beam Spectrum used in Testing

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Thus twenty-two tests provided the final data set for analysis. Current and voltage waveforms were highly reproducible, but both calorimetry and the test results suggest variation of as much as 20 percent from discharge to discharge. This was not so severe as to interfere with the interpretation of the experiment. It may have originated in the method of mounting and grounding the beam-mask, and this should be studied before further tests are conducted.

Based on fourteen calorimetry runs with the mask in place, the higher fluence averages out to 41.5 cal/cm$^2$, and the lower to 23.5 cal/cm$^2$. Weight measurements were performed on the samples, but were unreliable due to loss of adhesive and some chipping of the resin. Depth of removal measurements proved highly successful, and are reported here as the most accurate indication of actual mass removal. The craters were flat-bottomed to within a few tenths of a mil, with sharp sides and a true diameter of 0.50" ± .01. Depths of removal were measured both on center and at four points midway between the center and the crater rim. Fluences, impulses and depths of removal are summarized in Table III. The possibility that material was lost by front surface spall (caused by a trailing tensile pulse) rather than pure vaporization cannot be entirely ruled out. But the appearance of the crater bottoms strongly suggests local decomposition rather than mechanical fracture, and the measured depth losses are believed to be true indications of the material removal caused by the blowoff phenomena.

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## TABLE III

### EXPERIMENTAL DATA

| Sample Number | Type | Fluence Cal/cm$^2$ | Impulse kilotaps | Depth mils | Depth gm/cm$^2$ |
|---|---|---|---|---|---|
| 9 | A | 23.5 | 3.71 | 14.9 | .0494 |
| 10 | A | 23.5 | ---- | 15.9 | .0527 |
| 11 | A | 23.5 | 3.28 | 13.0 | .0431 |
| 41 | B | 23.5 | 3.48 | 14.0 | .0467 |
| 42 | B | 23.5 | ---- | 13.3 | .0444 |
| 43 | B | 23.5 | 3.48 | 13.5 | .0451 |
| 50 | B | 23.5 | 3.94 | 13.2 | .0441 |
| 32 | C | 23.5 | 5.07 | 13.7 | .0458 |
| 36 | C | 23.5 | 3.84 | 13.8 | .0461 |
| 40 | C | 23.5 | 3.63 | 13.1 | .0438 |
| 104 | SC-1008 | 23.5 | 3.63 | 13.1 | .0409 |
| 105 | SC-1008 | 23.5 | 3.14 | 15.0 | .0468 |
| 106 | SC-1008 | 23.5 | 2.66 | 13.7 | .0427 |
| 12 | A | 41.5 | 13.55 | 20.7 | .0686 |
| 14 | A | 41.5 | 12.02 | 20.0 | .0663 |
| 15 | A | 41.5 | 9.98 | 21.5 | .0713 |
| 55 | B | 41.5 | 14.94 | 20.2 | .0674 |
| 57 | B | 41.5 | 12.07 | 21.2 | .0708 |
| 59 | B | 41.5 | 13.20 | 18.9 | .0631 |
| 60 | B | 41.5 | ----- | 19.5 | .0651 |
| 34 | C | 41.5 | 12.02 | 18.8 | .0628 |
| 35 | C | 41.5 | 16.88 | 19.8 | .0662 |
| 37 | C | 41.5 | 17.49 | 20.6 | .0689 |
| 100 | SC-1008 | 41.5 | ----- | 20.8 | .0649 |
| 101 | SC-1008 | 41.5 | 6.39 | 21.3 | .0664 |
| 102 | SC-1008 | 41.5 | 6.35 | 20.3 | .0633 |
| 103 | SC-1008 | 41.5 | 5.83 | 20.9 | .0652 |

# SECTION IV

## DATA ANALYSIS

Calculation of blowoff impulses by BBAY theory requires only a knowledge
of the energy deposition profile, $E(u)$, the depth of vaporization, $u_v$, and
the function $E_n(E)$. The deposition profile was provided by Ion Physics
Corporation and is shown as a histogram in Figure 5. Depths in mass per
unit area can be calculated from measured depths and densities, and were
included in Table III. It remains to specify $E_n$ in some simple form which
incorporates parameters expected to correlate with the energy absorbed or
released by the material. However, this could not be undertaken until a
basic problem was resolved within the experimental data itself.

Making the assumption that vaporization is a local phenomenon, the
dose at the depth of incipient vaporization should be a constant for any
material. This was found not to be true for the data obtained in this
experiment. Figure 6 displays the deposition profiles and depths of removal
for shots 9 and 12. These shots were both on sample type A, but shot 9
was at the lower fluence and 12 at the higher fluence. One should notice
that the depths of removal lead to different incipient vaporization or
decomposition energies of the material for the two fluences. Less energy
was required for vaporization at the higher total fluence than at the lower.
This discrepancy is well outside experimental error and occurs for all of
the data. This forces the conclusion that either the deposition profile
has changed in going from one fluence to the other or that front surface
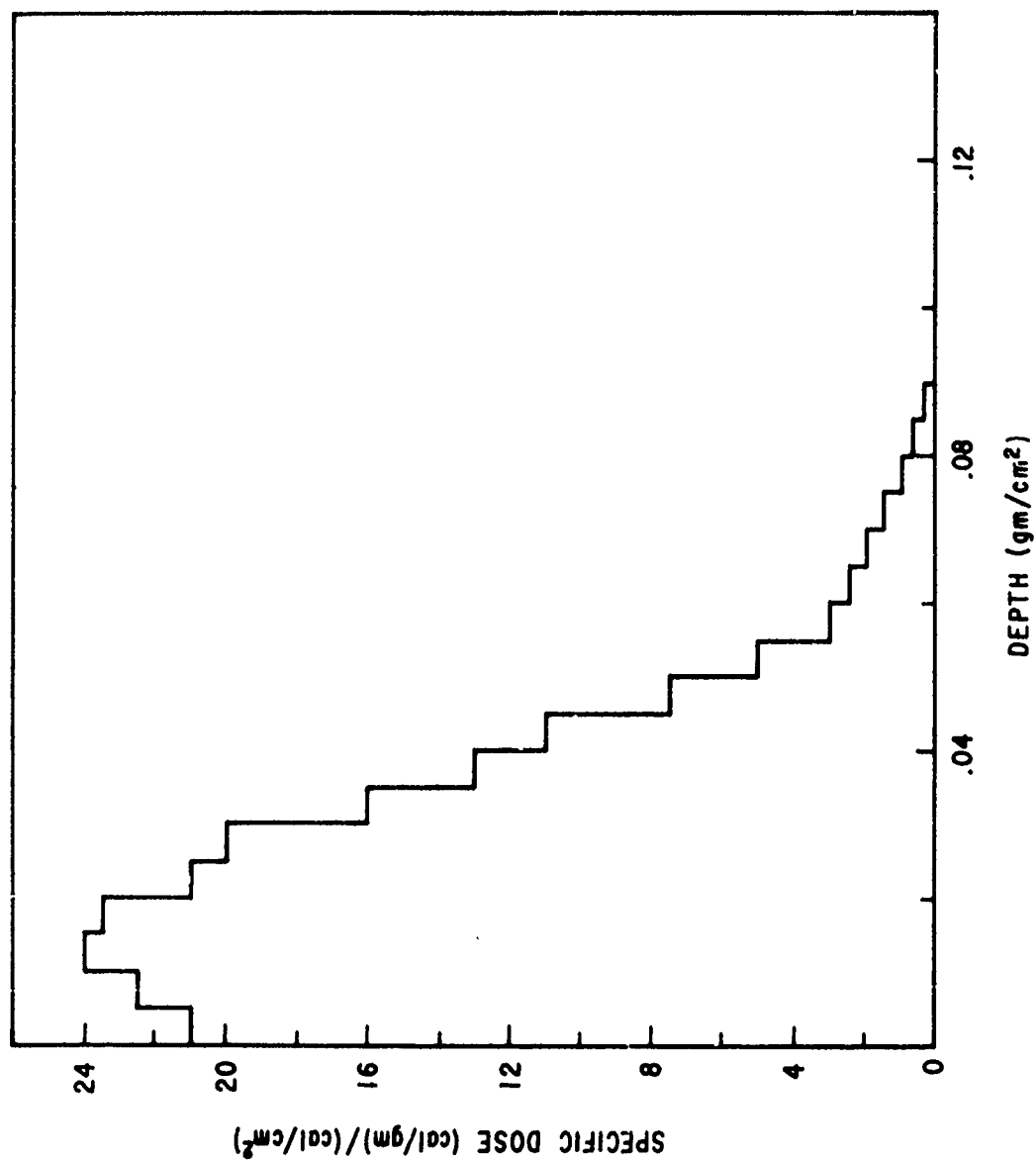spall has occurred. As stated before, the latter appears unreasonable.

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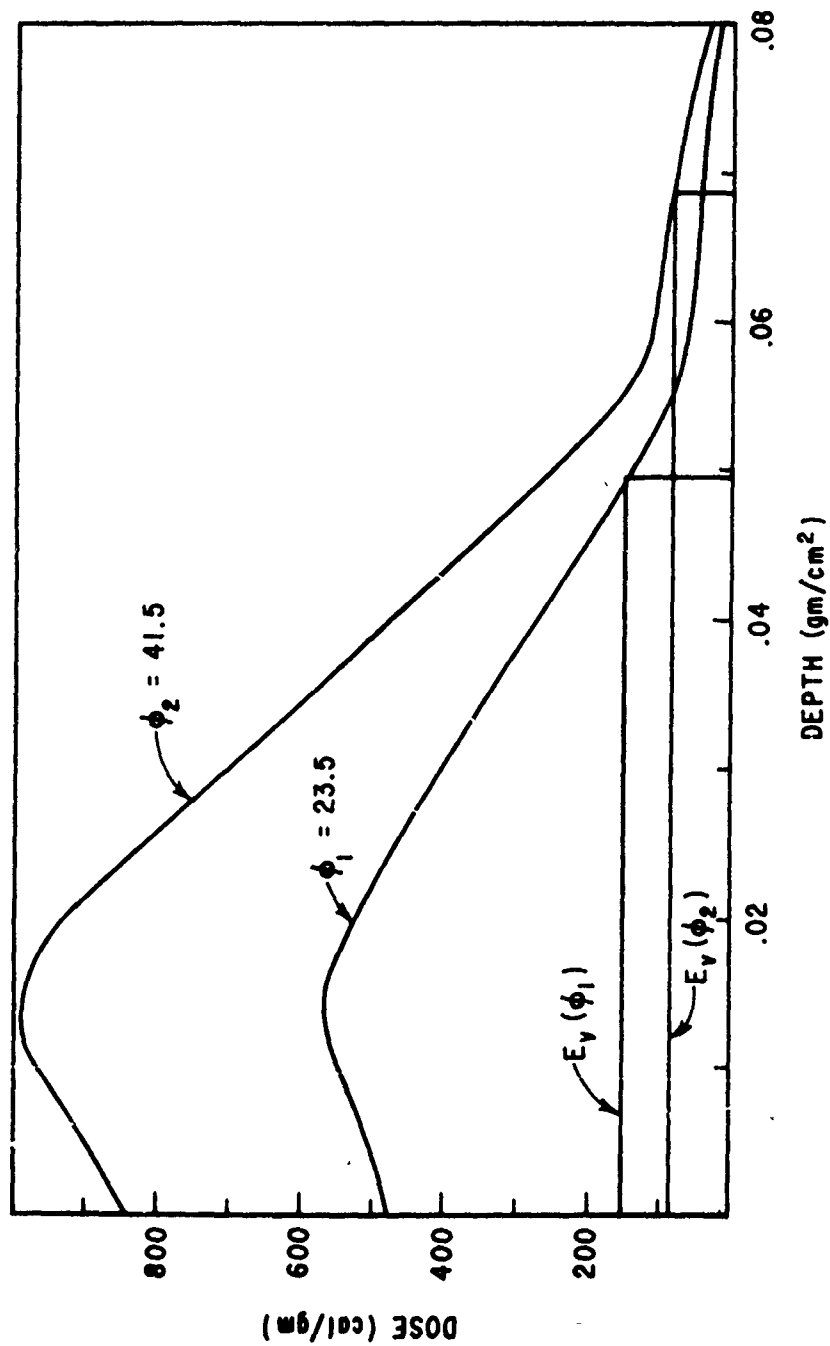Figure 5. Deposition Profile in Resin from Electron Beam

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Figure 6. Deposition Profiles and Depths of Removal for shots 9 and 12

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There appears to be two ways for the deposition profile to change. First, in raising the fluence and trying to keep the same spectrum, the mean electron incident angle will change. However, in going from 20 to 40 cal/cm$^2$, the change in the angle should be no more than 4 or 5°. The result of the change in this small angle is negligible and certainly inside the experimental errors. The second mechanism for changing the shape of the deposition profile would be that energy is transported somehow from shallow, high dose regions into deeper regions. Any complicated model for this transport process invokes myriad untestable assumptions and a prohibitive number of arbitrary parameters. Fortunately, every trial calculation, using any model, led to the same simple conclusion: By the time the transport of energy is sufficient to reconcile the vaporization energies at the two fluence levels, the effective dose profile has become an almost perfect half-Gaussian, $E = E_0 e^{-ku^2}$, characterized by just two parameters, $E_0$ and k. The factor k can be fixed by the required constancy in vaporization energy, and two values for $E_0$, corresponding to the two experimental fluence levels, then follow from the area under the Ion Physics histogram and the measured fluences.

Values for k can be calculated from each of the four sets of resin data, and the half-Gaussian model is corroborated by the excellent agreement among these values as seen in Table IV. The value k = 241.6 was adopted, leading to values for $E_0$ of 401.5 cal/gm and 708.9 cal/gm. This method is intended to say nothing about the mechanism involved in broadening

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the deposition profile. The effect, whatever its source, seems to be real
and should be sought in other experimental data. The final half-Gaussian
is shown as the smooth curve in Figure 7.

The assumption of a Gaussian deposition profile and constant vaporiza-
tion energy for each material is equivalent to the statement that the
difference between the squares of the vaporization depths at the two fluence
levels should be the same for all materials. These differences are given
in Table IV, and show only a small variation. The task of analyzing the
experimental results is greatly facilitated if the average depths of vapori-
zation for each material, at each fluence, are slightly adjusted so as to
make these differences truly constant at the mean value of .002354 $(gm/cm^2)^2$.
This can be done without changing any depth by more than 0.5 percent, which
is negligible compared to the precision of the measurements, and the only
purpose of the adjustment is to ensure mathematical consistency in the
later treatment of the data. The original and adjusted values are given
in Table IV.

A suitable expression for $E_n$ can now be adopted. At least two adjust-
able parameters are needed, one to fix the depth of vaporization and the
other to reflect the addition of removal of thermochemical energy. A third
parameter proved essential in order to fix the deposited energy at which
the chemical processes leading to the liberation or absorption of chemical
energy begin to be important. The final form for $E_n$ was:

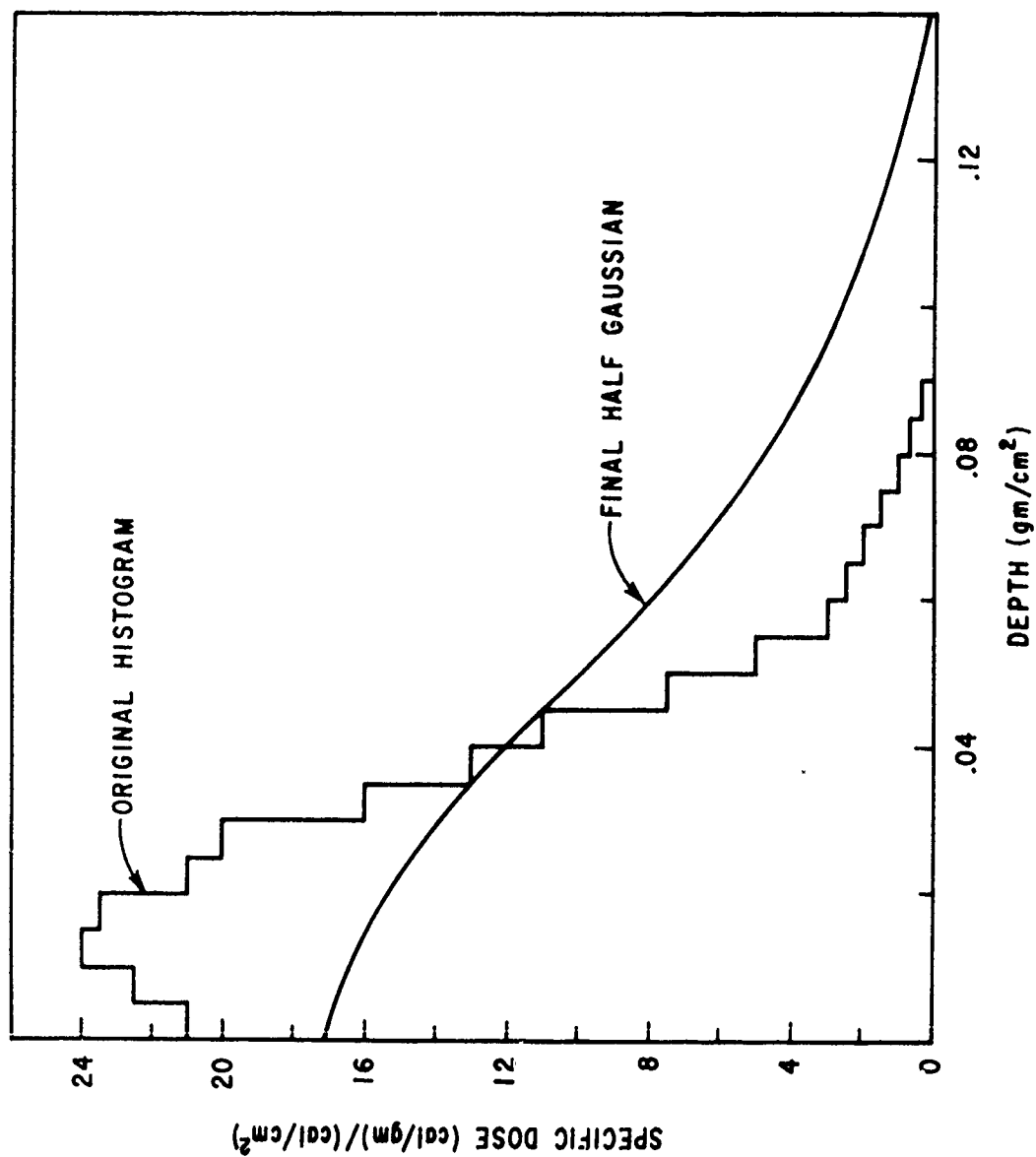$$E_n = E_v(1 + \ln\frac{E}{E_v}) \qquad\qquad \text{for E less than } E^*,$$

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Figure 7. Original and Final Deposition Profiles for the Resins from the Electron Beam

# TABLE IV

## Deposition and Vaporization Parameters

| Resin Type | Fluence | Average Depth u, $gm/cm^2$ | $u_2^2 - u_1^2$ $(gm/cm^2)^2$ | $k$ $(gm/cm^2)^{-2}$ | Adjusted Depth $gm/cm^2$ |
|---|---|---|---|---|---|
| A | Low | $u_1 = .0484$ | | | .04848 |
| | | | .002377 | 239 | |
| A | High | $u_2 = .0687$ | | | .06859 |
| B | Low | $u_1 = .0451$ | | | .04526 |
| | | | .002402 | 237 | |
| B | High | $u_2 = .0666$ | | | .06635 |
| C | Low | $u_1 = .0452$ | | | .04505 |
| | | | .002313 | 246 | |
| C | High | $u_2 = .0660$ | | | .06621 |
| SC-1008 | Low | $u_1 = .0435$ | | | .04338 |
| | | | .002320 | 245 | |
| SC-1008 | High | $u_2 = .0649$ | | | .06508 |
| | Final Average | | .002354 | 241.6 | |

and $\quad E_n = E_v(1 + \ln\frac{E}{E_v}) + \Delta E$ $\quad\quad\quad$ for E greater than $E^*$.

This expression departs very little from the standard logarithmic expression for $E_n$. The only modification is that, at some energy density $E^*$, new chemical processes emerge and add an amount $\Delta E$ to the logarithmic component. $E_v$ is of course the energy required to cause vaporization. Clearly this step-function is only an approximation to some smooth function, but the results are not very sensitive to the degree of rounding and further parameters were avoided.

Combination of this expression for $E_n$ with the Gaussian deposition profile leads to a situation in which the basic BBAY integral,

$$I^2 = 2.88 \int_0^{u_v} (E - E_n)u\,du \quad\quad\quad (1)$$

can be expressed in elementary functions. This was not used as a criterion in selecting E and $E_n$, but it greatly simplifies computation. If the momentum per unit area, I, is expressed in Kilodyne-sec/cm$^2$ and all energies are given in cal/gm, the integral is:

$$I^2 = \frac{60.28}{k}(E_o - E_v(1 + \ln\frac{E_o}{E_v} + \frac{1}{2}\ln^2\frac{E_o}{E_v}) - \Delta E \cdot \ln\frac{E_o}{E^*}) \quad\quad\quad (2)$$

Since k is a known constant, and I, $E_o$ and $E_v$ are known for each material and test, this expression can be solved for $E^*$ and $\Delta E$, for each resin, using the data from the two fluence levels. Specifically, if we write $E_o = E_1$, $I = I_1$ and $u_v = u_1$ at the lower fluence, and $E_o = E_2$, $I = I_2$ and $u_v = u_2$ at the higher, then:

$$\Delta E = \frac{E_2 - E_1}{\ln(E_2/E_1)} - E_v(1 + \ln\frac{E_2 E_1}{E_v}) - \frac{1}{60.28} \cdot \frac{I_2^2 - I_1^2}{u_2^2 - u_1^2} \quad\quad\quad (3)$$

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## TABLE V

### Parameters Associated with $E_n$

| Resin Type | $E_v$ cal/gm | $\Delta E$ cal/gm | $E^*$ cal/gm | $E_n^{min}$ cal/gm |
|---|---|---|---|---|
| A | 228 | -776 | 380 | -431 |
| B | 244 | -1069 | 385 | -714 |
| C | 247 | -1460 | 384 | -1104 |
| SC-1008 | 255 | -104 | 285 | +180 |

and E* can then be found by substituting back in Equation (2). The resulting values for $E_v$, $\Delta E$ and E* are given in Table V along with $E_n^{min}$, the value for $E_n$ just after the step-function drop.

The values for E* are all about 380 cal/gm for the modified resins, while that for SC-1008 is lower, 285 cal/gm. All the $\Delta E$'s are negative, corresponding to release of chemical energy into the blowoff system, but that for SC-1008 is much smaller than those for the modified resins.

The actual values for $\Delta E$ are surprisingly large, ranging from -104 cal/gm for SC-1008 to -1460 cal/gm for the most energy rich resin, type C. The magnitude of this step function depends almost entirely on the measured momentum values through the term proportional to $I_2^2 - I_1^2$ in Equation (3). If the measured momenta had all been lower by about 30 percent, the values for $\Delta E$ would have assumed the more expected values of a few hundred calories per gram. Very careful analysis of the experimental data provides no indication that the measured momenta might be too high by this amount; an anode debris correction could be applied to lower the low-fluence values by several hundred, but because of the uncertainty in its precise value, this correction was omitted, and in any case it is nowhere near sufficient to have much effect toward lowering the values for $\Delta E$. The high momenta observed therefore remain as probably correct, and an explanation would have to be sought through further ballistic experiments. The actual $E_n$ functions derived may be seen in Figure 8.

There is a strong correlation between the calculated $\Delta E$ values and the thermodynamic parameters for the modified resins. This is shown in
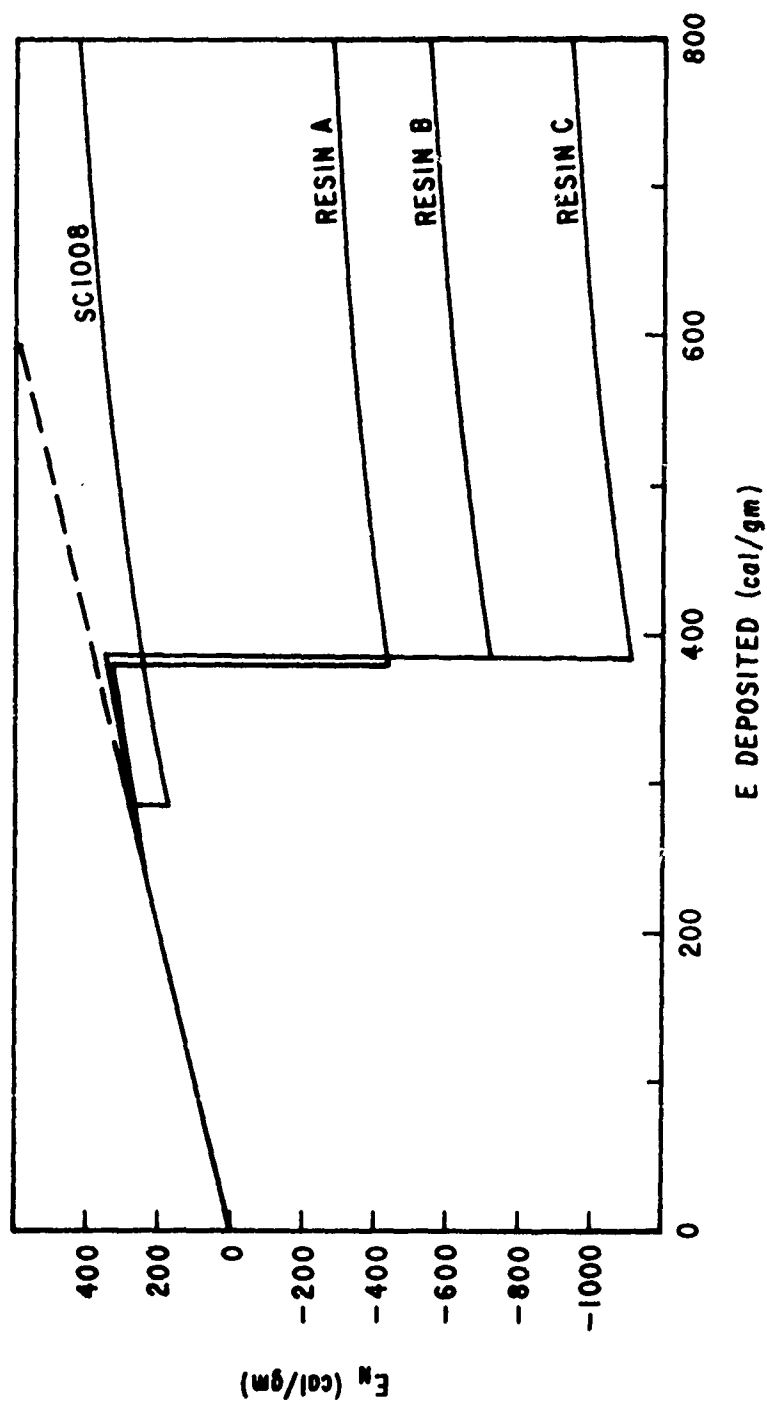
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Figure 8. The Derived $E_n$ Functions for the Tested Resins

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Figures 9 and 10. The upper points and line represent $E_n^{min}$ of the resins plotted versus their $E_{H_2O}$ and $E_{CO}$, respectively. The lower points and line represent the $\Delta E$ of the resins versus their $E_{H_2O}$ and $E_{CO}$, respectively. The fact that the lines are not at a 45° slope indicates that uniform products were not obtained from all of the modified resins. SC-1008 does not follow this correlation, suggesting that its higher carbon content is somehow important in determining the energetics of decomposition. It would seem profitable to apply this simple type of $E_n$ function to the analysis of data from a much wider variety of resin systems. Efforts to correlate the quantities $E_v$, $E^*$ and $\Delta E$ with sample composition and thermochemistry would have a vastly better chance of success than any correlation attempt based only on total momentum values.
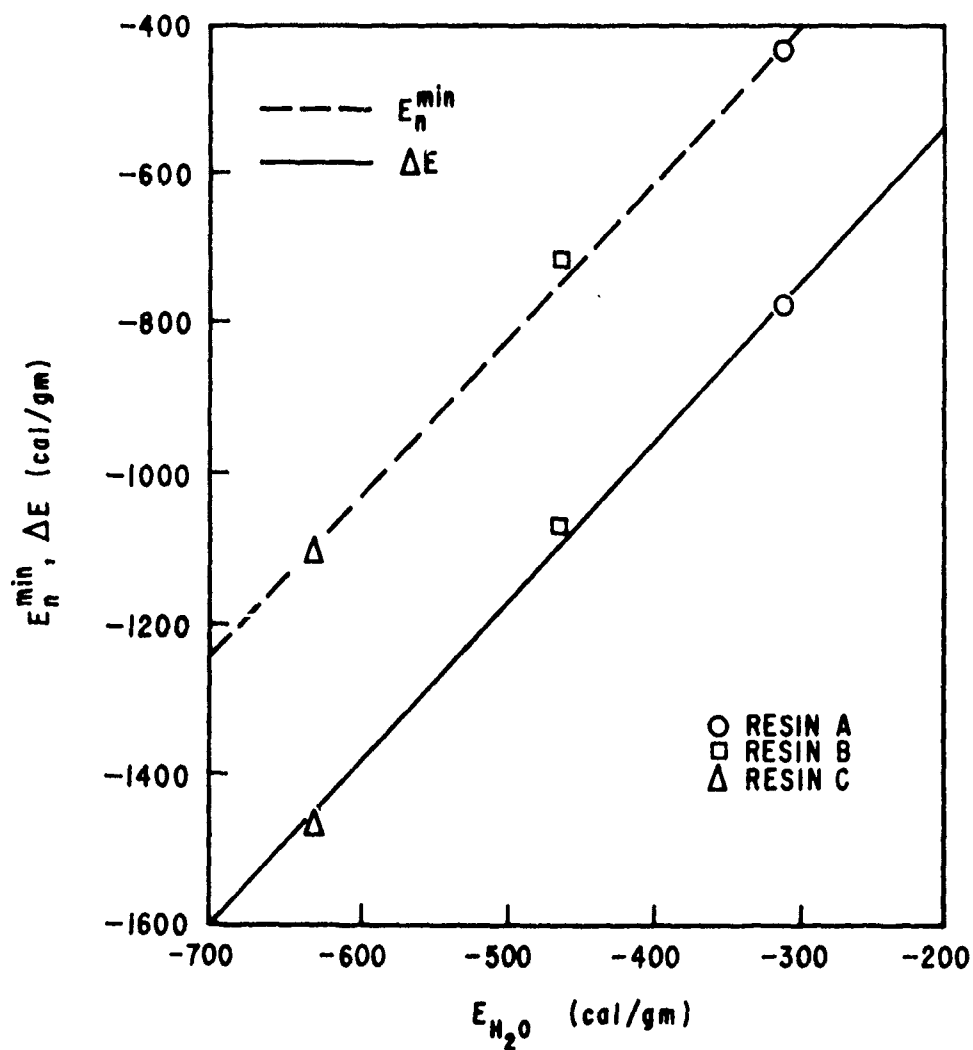
Figure 9.  Comparison of Calculated $\Delta E$ and $E_n^{min}$ Values versus Experimental $E_{H_2O}$ Values
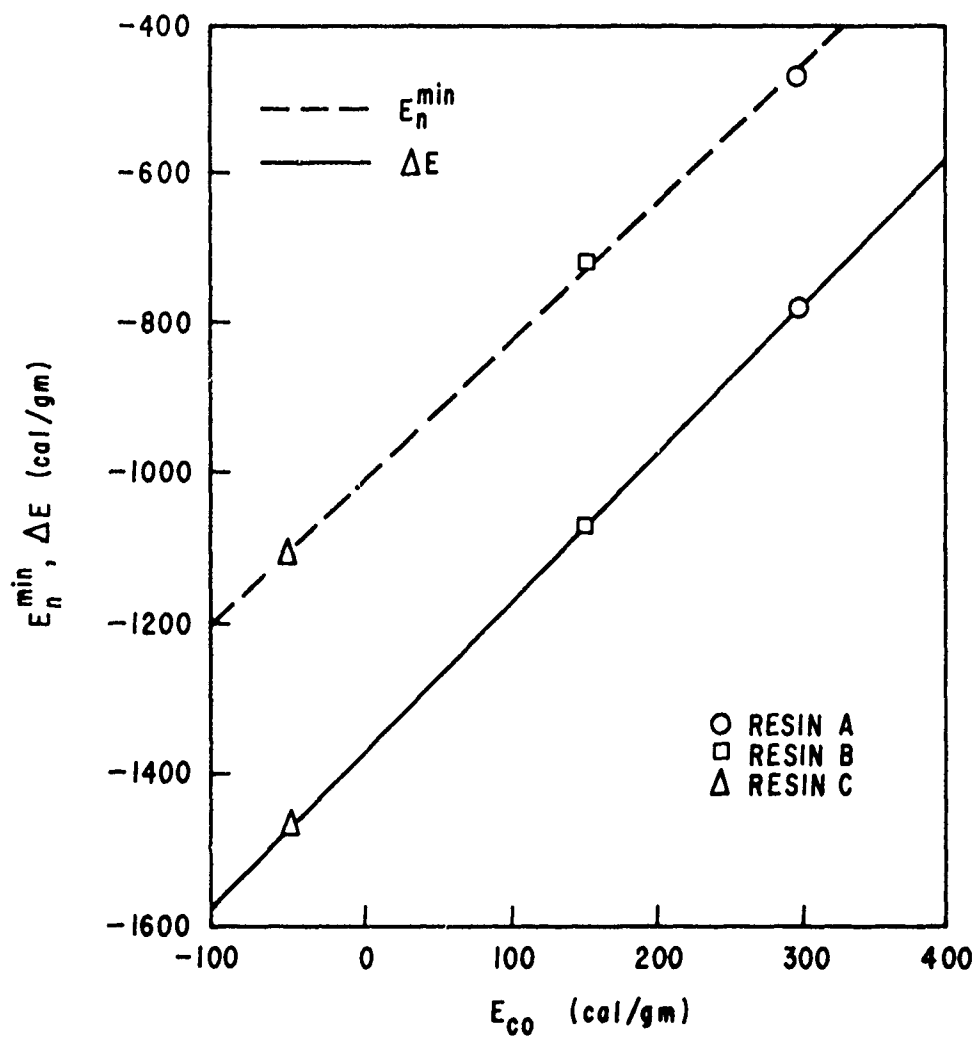
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Figure 10.   Comparison of Calculated $\Delta E$ and $E_n^{min}$ Values
versus Experimental $E_{CO}$ Values

# SECTION V

## CONCLUSIONS

To obtain consistent values for sample vaporization energy, one had to assume either front surface spall or energy transport within the samples at early times, which broadens the deposition curve into a half-Gaussian. Examination of the samples leads to the acceptance of the second assumption.

A simple logarithmic expression for $E_n$, modified by a step-function to represent the onset of thermochemical effects, is entirely adequate to give good agreement between experiment and BBAY theory.

The parameters specifying $E_n$ correlate strongly with measured thermochemical parameters, at least for materials of similar composition.

All resins studied decompose exothermically, and the magnitude of the energy release suggests the formation of highly stable species such as water.

# SECTION VI

## RECOMMENDATIONS

The conclusions should be more exhaustively analyzed by parallel studies of blowoff thermodynamics and kinetics.

The techniques developed here should be applied to a large number and variety of resins.

The mechanisms which result in a lack of correlation between energy of decomposition and depth of removal should be investigated.

$E_n$ functions of the kind used in this study should be incorporated into standard blowoff codes to allow empirical adjustment of $E_v$, $E^*$ and  E as part of routine experimental analysis.

Detailed elemental and thermochemical analysis should be conducted on all presently important resins and composites, and such analysis should be adopted as part of production and quality controls.

A combined experimental and theoretical program should be undertaken specifically to develop low impulse resins on the basis of thermochemical properties.

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**13 ABSTRACT**

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Demonstration of a clear correlation between measurable thermodynamic properties and the impulsive momentum developed during blowoff would place predictive techniques on a more secure foundation and might make possible the formulation of resins with thermochemical properties specifically chosen for minimum blowoff damage. To find such a correlation, a set of modified phenolic resins was prepared which had similar elemental compositions and physical properties, but which differed strongly in their thermochemical parameters. Exposure of these samples on the Ion Physics Corporation Neptune B electron facility, with measurement of impulse by ballistic pendulum, yielded data which displayed a linear correlation between heats of decomposition and an additive term in the $E_n$ function derived from measured impulses through simple BBAY theory. Evidence was also found for a broadening of the electron deposition profile at early times. The techniques developed here are applicable to a larger set of sample materials, and particularly to resins of more practical interest.

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| Blowoff | | | | | | |
| Phenolic resin | | | | | | |
| Electron beam | | | | | | |